

# Photochemistry of CO and H<sub>2</sub>O: Analysis of Laboratory Experiments and Applications to the Prebiotic Earth's Atmosphere

JUN-SHAN WEN,<sup>1</sup> JOSEPH P. PINTO,<sup>2</sup> YUK L. YUNG

*Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena*

The role photochemical reactions in the early Earth's atmosphere played in the prebiotic synthesis of simple organic molecules was examined. We have extended an earlier calculation of formaldehyde production rates to more reduced carbon species, such as methanol, methane, and acetaldehyde. We have simulated the experimental results of Bar-Nun and Chang (1983) as an aid in the construction of our photochemical scheme and as a way of validating our model. Our results indicate that some fraction of CO<sub>2</sub> and H<sub>2</sub> present in the primitive atmosphere could have been converted to simple organic molecules. The exact amount is dependent on the partial pressure of CO<sub>2</sub> and H<sub>2</sub> in the atmosphere and on what assumptions are made concerning the shape of the absorption spectra of CO<sub>2</sub> and H<sub>2</sub>O. In particular, the results are most sensitive to the presence or absence of absorption at wavelengths longward of 2000 Å. We also find that small quantities of CH<sub>4</sub> could have been present in the prebiotic Earth's atmosphere as the result of the photoreduction of CO.

## INTRODUCTION

The composition of the Earth's atmosphere prior to the origins of life, and the possible role that the atmosphere may have played in the production of simple organic molecules, have long been the subject of intense debate. Numerous experiments have been designed to simulate the atmospheric chemistry of various assumed compositions for a variety of energy sources. *Garrison et al.* [1951] had used a composition reflecting the oxidation state of modern volcanic gases (today, carbon and nitrogen are present mainly as CO<sub>2</sub> and CO and as N<sub>2</sub>, respectively). *Miller* [1953], in his experiments, simulated lightning discharges in an atmosphere in which carbon and nitrogen were present as methane and ammonia, respectively, and found a much wider range of organic compounds, including amino acids. The needed reducing atmosphere would have been possible if volcanic gases were allowed to equilibrate with native iron in the upper mantle. Once the Earth's core and mantle had differentiated, however, iron and other siderophiles would have been sequestered in the core, and the redox state of volcanic gases should have been much closer to what is observed today. *Stevenson* [1983] suggested that differentiation was an ongoing process occurring during the accretion of the earth from planetesimals. The accretionary phase of the Earth's history probably lasted for a time of the order of 10<sup>5</sup> years, certainly no more than 5 × 10<sup>8</sup> years. During the early stages of accretion, degassed volatiles were probably more reducing than afterward, because of equilibration of the gases with iron in infalling meteorites [*Ringwood*, 1979]. It is not clear at what stage of Earth history the synthesis of organic

molecules occurred. Conditions were least favorable for the preservation of organic molecules during the early phases of accretion because of high surface temperatures. Conditions were more favorable after the surface had cooled sufficiently to allow the presence of a stable solid crust and of liquid oceans. These conditions were certainly met prior to 3.8 billion years ago, as shown by the existence of sedimentary rocks in the Isua formation. The oldest unambiguous evidence of life are fossiliferous stromatolites of about 3.5 billion years age [*Lowe*, 1980; *Walter et al.*, 1980], and it is possible that some of the kerogens found in the Isua formation are biogenic [*Schopf et al.*, 1983].

Biological emissions are the primary source of methane to the modern atmosphere (see *Khalil and Rasmussen* [1983], for example). Much smaller quantities are emitted by submarine hot springs. This methane must come from a deep primordial reservoir since it is associated with high concentrations of <sup>3</sup>He [*Craig and Lupton*, 1976]. It is extremely difficult to estimate fluxes of CH<sub>4</sub> associated with submarine hydrothermal activity on the early Earth. We will assume for the present study that the ratio of this flux of carbon to the surface to that of CO<sub>2</sub> and CO on the early Earth was the same as the modern value, because there is not any strong evidence to suggest that the composition of volcanic volatiles has changed significantly since the time of the oldest known rocks, 3.8 billion years ago [*Holland*, 1984]. Because of the uncertain redox state of volcanic gases prior to this time, laboratory investigations which are based on a variety of atmospheric compositions are all useful. Indeed, they all may have some relevance for understanding the role of the atmosphere in the abiotic synthesis of organic molecules, because the composition of Earth's atmosphere may have rapidly evolved from a reduced state to a more oxidizing one, during accretion. They can also contribute to our understanding of a number of key chemical processes.

The laboratory experiments of *Hubbard et al.* [1971], *Bar-Nun and Hartman* [1978], and *Bar-Nun and Chang* [1983] have shown that the gas phase photolysis of H<sub>2</sub>O in the presence of CO could lead to the production of simple organic molecules of potential importance for the abiotic synthesis

<sup>1</sup>Now at Department of Chemistry, University of California, San Diego, La Jolla.

<sup>2</sup>Now at Geophysical Fluid Dynamics Laboratory, Princeton University, Princeton, New Jersey.

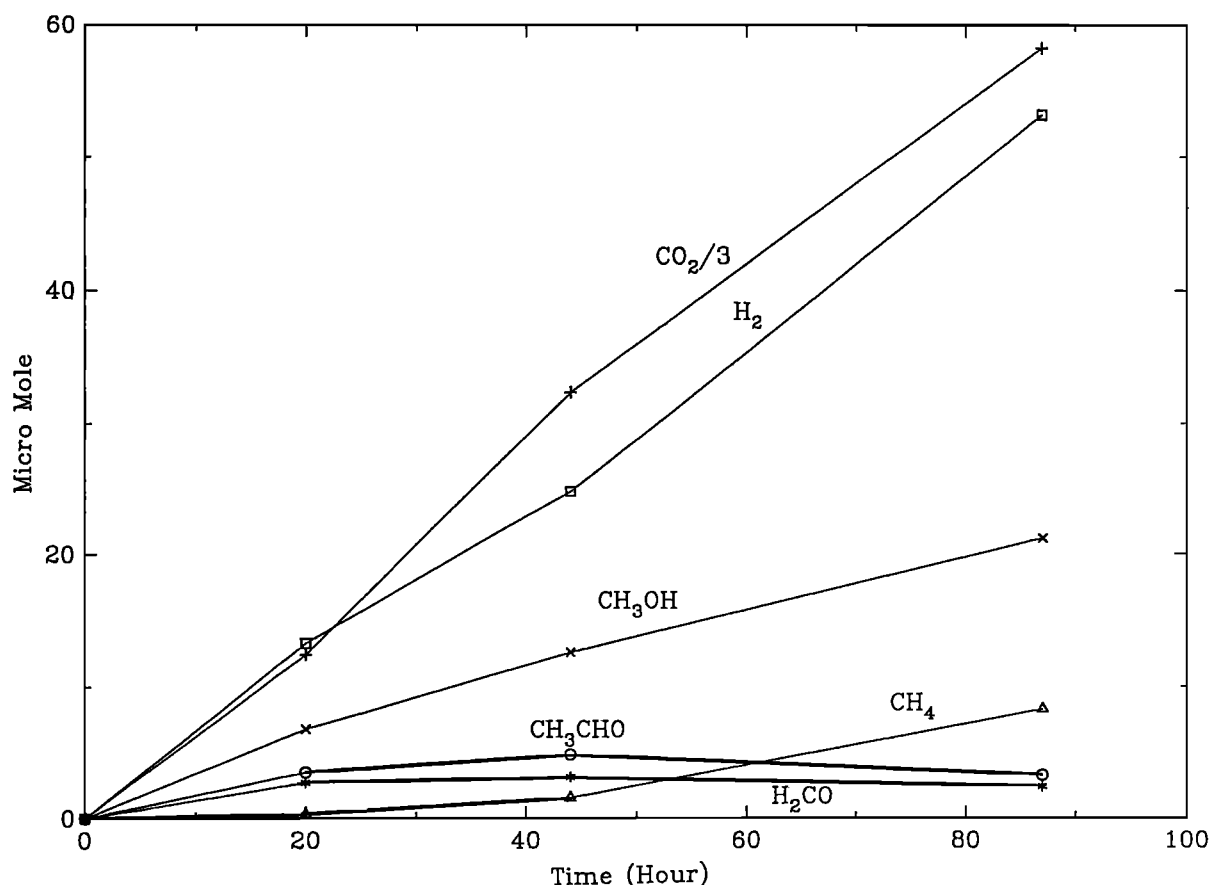


Fig. 1. The time evolution of the major products in the experiments (runs 9–11) of Bar-Nun and Chang [1983].

of more complex compounds. Bar-Nun and Chang found a range of reduced carbon compounds, such as aldehydes, alcohols, alkanes, and alkenes, resulting from the hydrogenation of CO. Their experiments are especially useful in that they provide quantitative data for developing and testing kinetic mechanisms, although they did not attempt to do this themselves.

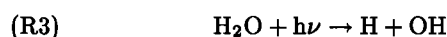
The present work will be composed of a numerical simulation of the experimental results of Bar-Nun and Chang and a modeling study of the chemistry of the prebiotic Earth. The modeling study will address the relevance of the experimental results for the prebiotic Earth and the reactions that might have been important for the production of simple organic molecules in the atmosphere. The present study will extend our earlier modeling efforts (Pinto *et al.*, [1980]; hereafter referred to as paper 1) to include new reactions for the reduction of formaldehyde to methanol and methane. Because of uncertainties in the abundance of major constituents, such as CO<sub>2</sub> and H<sub>2</sub>, the calculations will be performed for a wide range of H<sub>2</sub> and CO<sub>2</sub> concentrations.

#### ANALYSIS OF EXPERIMENTAL RESULTS

Bar-Nun and Chang [1983] continuously irradiated mixtures of CO and H<sub>2</sub>O in varying proportions at 1849 Å and monitored the buildup of products. In the experiments we will analyze (their runs 9–11), the partial pressure of CO was 300 torr. The amount of water vapor was the equivalent of 0.03 mL of liquid water. Temperature in the reaction

vessel was held fixed at 59°C, and the irradiation time varied from 20 to 87 hours in these experiments. The evolution of the products in their experiments 9–11 is shown in Figure 1. The major reaction products are CO<sub>2</sub> and H<sub>2</sub>, followed by CH<sub>3</sub>OH, H<sub>2</sub>CO, and CH<sub>4</sub>. Smaller quantities of C<sub>2</sub> hydrocarbons, such as acetaldehyde, ethanol, and ethane were also found. The results of our simulation of the major molecules formed in this experiment are shown in Figure 2a. The concentrations of free radicals we have calculated are shown in Figure 3. Their abundances are generally small, and they were not measured in the experiments because the analysis was performed at the end of the experiment, when they had already been recombined.

Table 1a lists the photodissociation reactions used in the simulation of the experiments. The optical depth in the reaction vessel is estimated from the measured evolution of CO<sub>2</sub>. This value is then used in the calculation of photolysis rates. The reactions and their rate coefficients used in the calculations are shown in Table 1b. The sequence of reactions we propose to explain the production of methane in their reaction vessel is as follows. Since CO does not absorb at 1849 Å, it was the photolysis of water vapor which initiated the chemistry occurring in the experiment,



and



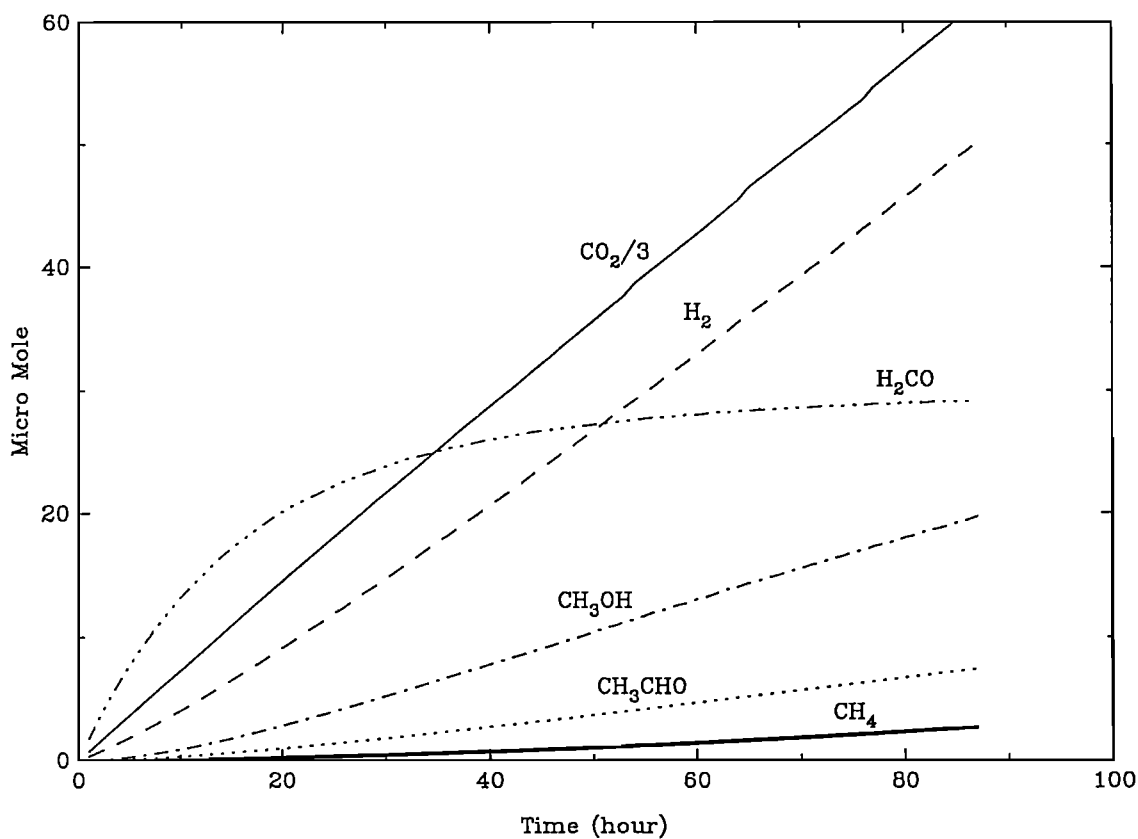


Fig. 2a. Results of our model simulation of the experimental data shown in Figure 1. The reaction set used is given in Tables 1a and 1b.

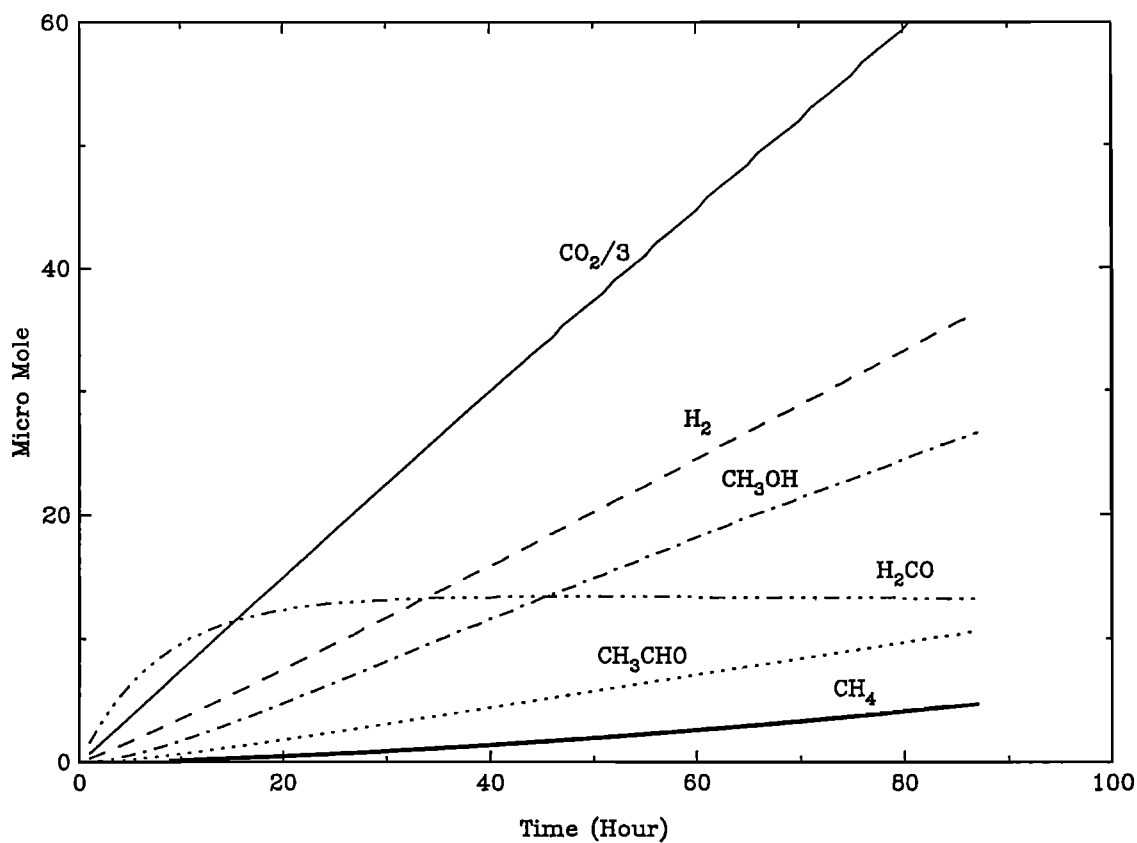


Fig. 2b. Same as Figure 2a, except  $k_{69} = 1 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ .

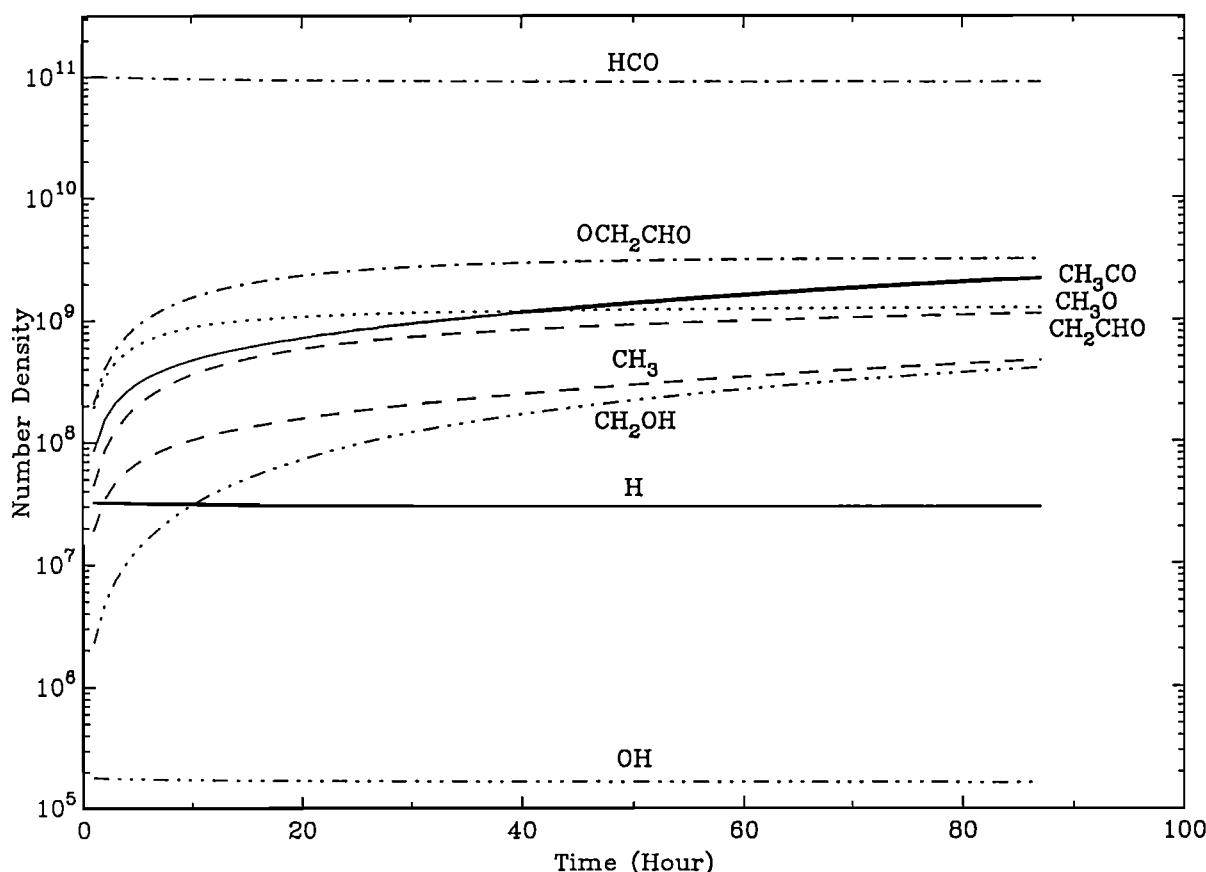
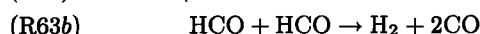
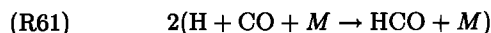
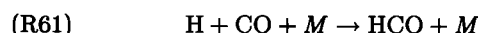
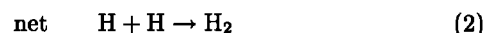
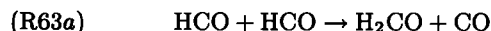


Fig. 3. Calculated concentrations of the free radicals in the model simulation of the experiment. For comparison with Figures 2a and 2b, we note that  $1 \times 10^{11}$  molecules equals  $1.7 \times 10^{-4}$   $\mu\text{mol}$ .

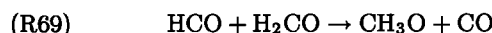
The hydrogen atoms can recombine with CO to yield formyl radicals via



The formyl radicals then disproportionate to produce formaldehyde,



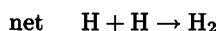
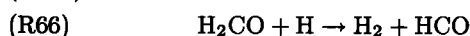
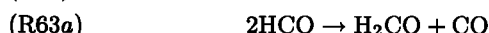
Another possibility is that formyl radicals were reacting with formaldehyde to yield methoxy radicals,



There are at least four different pathways by which the addition of hydrogen to formaldehyde can occur. Hydrogen atoms can be added directly in the reaction,



Using values for the rate coefficient of (R67a) estimated by Yung *et al.* [1988], it can be seen from Figure 3 that the concentration of H atoms is too small for (R67a) to be an effective source of compounds more reducing than formaldehyde. The concentration of H atoms is kept low by the following catalytic cycles:



(1)

However, Veyret and Lescaux [1981] have measured an upper limit of  $10^{-17} \text{ cm}^3 \text{ s}^{-1}$  for this reaction at room temperature. This reaction probably has an appreciable activity energy barrier, though. In this case, the rate coefficient at 59°C may be much larger than the room temperature value. Choosing an A factor of  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$  yields an activation energy of about 8.2 kcal mol<sup>-1</sup>. At 59°C the rate coefficient could be  $3.8 \times 10^{-17}$ , which has been used in the simulation. Results presented in Figure 2a show that the rate coefficient for (R69) is still not large enough to account for the reduction of formaldehyde observed in the experiments. Note that (R69) is the dominant source of CH<sub>3</sub>O in our simulation, the contribution from (R67a) being negligible. Figure 2b presents results of a model with a higher value for the rate coefficient of (R69),  $k_{69} = 1 \times 10^{-16}$ . This improves the agreement between the observed and computed H<sub>2</sub>CO but degrades that of H<sub>2</sub>. The overall agreement between

TABLE 1a. The Reactions and Their Coefficients Used Only in the Simulation of the Experiments of *Bar-Nun and Chang* [1983]

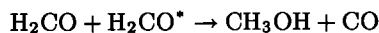
| Reaction No. | Reaction                                                                                   | Rate Constant          | Reference |
|--------------|--------------------------------------------------------------------------------------------|------------------------|-----------|
| (R3)         | $\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$                               | $7.13(-8)$             | a         |
| (R7a)        | $\text{H}_2\text{CO} + h\nu \rightarrow \text{HCO} + \text{H}$                             | $3.07(-7)$             | b         |
| (R7b)        | $\text{H}_2\text{CO} + h\nu \rightarrow \text{CO} + \text{H}_2$                            | $3.07(-7)$             | b         |
| (R8a)        | $\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3 + \text{OH}$                          | $7.68(-8)$             | c         |
| (R8c)        | $\text{CH}_3\text{OH} + h\nu \rightarrow \text{H}_2\text{CO} + \text{H}_2$                 | $3.12(-7)$             | c         |
| (R8d)        | $\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3\text{O} + \text{H}$                   | $3.12(-7)$             | c         |
| (R9a)        | $\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3 + \text{HCO}$                        | $3.07(-7)$             | d         |
| (R9b)        | $\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_4 + \text{CO}$                         | $3.07(-7)$             | d         |
| (R10)        | $\text{OCH}_3\text{CHO} + h\nu \rightarrow \text{CH}_2\text{CHO} + \text{OH}$              | $6.25(-7)$             | d         |
| (R95)        | $\text{CH}_3\text{CO} + \text{OH} + (M) \rightarrow \text{CH}_3\text{COOH} + (M)$          | $5.0(-11)$             | e         |
| (R96)        | $\text{CH}_3\text{CO} + \text{CH}_3 + (M) \rightarrow \text{CH}_3\text{COCH}_3 + (M)$      | $6.7(-9) T^{-0.8}$     | f         |
| (R97)        | $\text{CH}_2\text{OH} + \text{CH}_3 + (M) \rightarrow \text{C}_2\text{H}_5\text{OH} + (M)$ | $2.0(-11)$             | g         |
| (R98)        | $\text{HCO} + \text{H}_2\text{CO} + (M) \rightarrow \text{OCH}_2\text{CHO} + (M)$          | $3.8(-17)$             | e         |
| (R99)        | $\text{OCH}_2\text{CHO} + \text{HCO} \rightarrow \text{OCH}_3\text{CHO} + \text{CO}$       | $1.5(-10)$             | e         |
| (R100)       | $\text{OCH}_2\text{CHO} + \text{CO} \rightarrow \text{CH}_2\text{CHO} + \text{CO}_2$       | $2.6(-11) e^{-5940/T}$ | e         |
| (R101)       | $\text{OCH}_3\text{CHO} + \text{H} \rightarrow \text{CH}_2\text{CHO} + \text{H}_2\text{O}$ | $2.2(-12) e^{-2600/T}$ | e         |
| (R102)       | $\text{CH}_2\text{CHO} + \text{HCO} \rightarrow \text{CH}_3\text{CHO} + \text{CO}$         | $2.0(-10)$             | e         |

The photodissociation coefficients (per second) are computed for wavelength = 1849 Å. The rate coefficients are in units of  $\text{cm}^3 \text{s}^{-1}$ . Read  $7.13(-8)$  as  $7.13 \times 10^{-8}$ .

References: a, *Lee and Suto* [1986]; b, *L. C. Lee*, private communication, 1987, branching ratios are estimated; c, *Nee et al.* [1985], branching ratios are estimated; d,  $J_{9a} = J_{7a}$ ;  $J_{9b} = J_{7b}$ ;  $J_{10} = J_8$ ; e, Estimated; f, *Tsang and Hampson* [1986]; g, *Tsang* [1987].

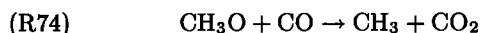
the experiment and our simulation for the most important species is fairly good.

Bar-Nun and Chang suggested the reaction

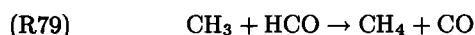


based on the experimental work of *Sodeau and Lee* [1978], who observed this reaction in a solid matrix of formaldehyde at 15 K. Because of the high concentration of quenching gases ( $\text{CO}$ ,  $\text{H}_2\text{O}$ ) compared to  $\text{H}_2\text{CO}$  in Bar-Nun and Chang's experiments, this reaction will be unimportant for a quenching rate coefficient greater than  $10^{-14} \text{ cm}^3 \text{s}^{-1}$ . The remaining possibility is that heterogeneous reactions were playing a major role. Although Bar-Nun and Chang varied the surface area of their reaction vessel by several orders of magnitude, by covering the walls with glass wool, there were not major changes in the products. However, this does not prove that heterogeneous reactions did not take place. For instance, heterogeneous reaction could have been initiated by ultraviolet radiation. In this case, the rate of the hydrogenation of formaldehyde would have been photon limited, rather than surface area limited. Further laboratory work is obviously needed to resolve these questions. Therefore we have omitted any consideration of heterogeneous phase chemistry in our analyses of the laboratory experiments or the primitive atmosphere.

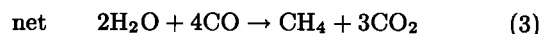
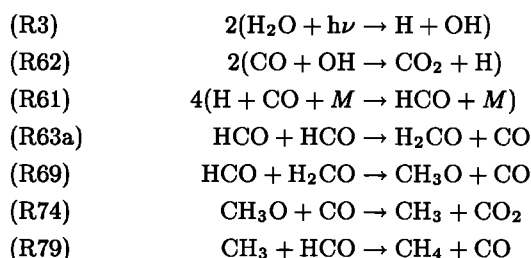
Once methoxy radicals have been formed, they can then react with  $\text{CO}$  to yield methyl radicals,



Methyl radicals can abstract hydrogen from the formyl radical according to

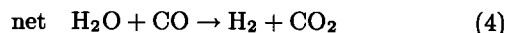
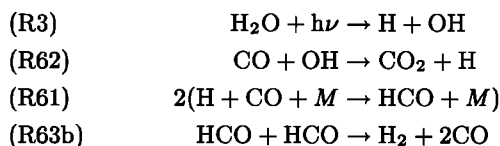


The combined effect of the above reactions can be written as



Although we have written the methoxy radical as the product for (R67a) and (R69), the formation of another isomeric form, namely, the hydroxymethyl radical ( $\text{CH}_2\text{OH}$ ) also occurs. We have adopted an equal probability for the formation of both products in the addition of  $\text{H}$  to  $\text{H}_2\text{CO}$  (R67b), since their formation involves approximately the same change in free energy.

The most abundant products formed in the laboratory experiments were  $\text{CO}_2$  and  $\text{H}_2$ . Their buildup could be described by the following reaction sequence:



In other words, UV photons catalyzed the attainment of equilibrium of the water gas reaction in the reaction vessel.

TABLE 1b. Chemical Reaction Used in Both the Laboratory Simulation Study and Atmospheric Modeling, With Their Preferred Rate Coefficients

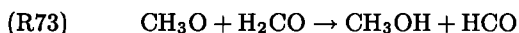
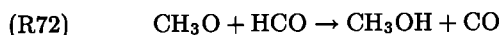
| Reaction No. | Reaction                                                                                             | Rate Constant                             | Reference    |
|--------------|------------------------------------------------------------------------------------------------------|-------------------------------------------|--------------|
| (R61)        | $\text{CO} + \text{H} + M \rightarrow \text{HCO} + M$                                                | $2.0(-33) e^{-850/T}$                     | a            |
| (R62)        | $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$                                           | $1.50(-13)(1 + 0.6P \text{ (atm)})$       | b            |
| (R63a)       | $2\text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO}$                                            | $3.0(-11)$                                | c            |
| (R63b)       | $2\text{HCO} \rightarrow \text{H}_2 + 2\text{CO}$                                                    | $5.0(-12)$                                | c            |
| (R64)        | $\text{HCO} + \text{H} \rightarrow \text{H}_2 + \text{CO}$                                           | $2.0(-10)$                                | c            |
| (R65)        | $\text{HCO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO}$                                  | $5.0(-11)$                                | c            |
| (R66)        | $\text{H}_2\text{CO} + \text{H} \rightarrow \text{H}_2 + \text{HCO}$                                 | $3.64(-16) T^{1.77} e^{-1510/T}$          | c            |
| (R67a)       | $\text{H}_2\text{CO} + \text{H} + (M) \rightarrow \text{CH}_3\text{O} + (M)$                         | $3.0(-16)$                                | d            |
| (R67b)       | $\text{H}_2\text{CO} + \text{H} + (M) \rightarrow \text{CH}_2\text{OH} + (M)$                        | $3.0(-16)$                                | d            |
| (R68)        | $\text{H}_2\text{CO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$                        | $5.7(-15) T^{1.18} e^{225/T}$             | c            |
| (R69)        | $\text{H}_2\text{CO} + \text{HCO} \rightarrow \text{CH}_3\text{O} + \text{CO}$                       | $3.8(-17)$                                | e (see text) |
| (R70)        | $\text{CH}_3\text{O} + \text{H} \rightarrow \text{H}_2\text{CO} + \text{H}_2$                        | $3.3(-11)$                                | c            |
| (R71)        | $\text{CH}_3\text{O} + \text{OH} \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}$               | $3.0(-11)$                                | c            |
| (R72)        | $\text{CH}_3\text{O} + \text{HCO} \rightarrow \text{CH}_3\text{OH} + \text{CO}$                      | $1.5(-10)$                                | c            |
| (R73)        | $\text{CH}_3\text{O} + \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} + \text{HCO}$            | $1.7(-13) e^{-1500/T}$                    | c            |
| (R74)        | $\text{CH}_3\text{O} + \text{CO} \rightarrow \text{CH}_3 + \text{CO}_2$                              | $2.6(-11) e^{-5940/T}$                    | c            |
| (R75a)       | $\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_3\text{O} + \text{H}_2$                       | $7.04(-18) T^{2.1} e^{-2450/T}$           | f            |
| (R75b)       | $\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_2\text{OH} + \text{H}_2$                      | $2.82(-17) T^{2.1} e^{-2450/T}$           | f            |
| (R76a)       | $\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}$             | $8.8(-12) e^{-798/T}$                     | g            |
| (R76b)       | $\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}$              | $2.2(-12) e^{-798/T}$                     | g            |
| (R77)        | $\text{CH}_3\text{OH} + \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH} + \text{CH}_3\text{OH}$ | $5.0(-13) e^{-2050/T}$                    | f            |
| (R78)        | $\text{CH}_3 + \text{H} + M \rightarrow \text{CH}_4 + M$                                             | $k_0 = 1.7(-27)$<br>$k_\infty = 1.5(-10)$ | h            |
| (R79)        | $\text{CH}_3 + \text{HCO} \rightarrow \text{CH}_4 + \text{CO}$                                       | $2.0(-10)$                                | c            |
| (R80)        | $\text{CH}_3 + \text{HCO} + (M) \rightarrow \text{CH}_3\text{CHO} + (M)$                             | $3.0(-11)$                                | c            |
| (R81)        | $\text{CH}_3 + \text{H}_2\text{CO} \rightarrow \text{CH}_4 + \text{HCO}$                             | $9.2(-21) T^{2.81} e^{-2950/T}$           | c            |
| (R82)        | $\text{CH}_3 + \text{CO} + M \rightarrow \text{CH}_3\text{CO} + M$                                   | $3.98(-10) T^{-7.56} e^{-5490/T}$         | c            |
| (R83)        | $2\text{CH}_3 + (M) \rightarrow \text{C}_2\text{H}_6 + (M)$                                          | $1.68(-9) T^{-0.64}$                      | c            |
| (R84)        | $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$                                        | $3.73(-20) T^3 e^{-4406/T}$               | c            |
| (R85)        | $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$                               | $3.2(-19) T^{2.4} e^{-1060/T}$            | c            |
| (R86)        | $\text{CH}_3\text{CO} + M \rightarrow \text{CH}_3 + \text{CO} + M$                                   | $1.45(19) T^{-8.62} e^{-11284/T}$         | c            |
| (R87)        | $\text{CH}_3\text{CO} + \text{H} \rightarrow \text{CH}_3 + \text{HCO}$                               | $1.6(-10)$                                | c            |
| (R88)        | $\text{CH}_3\text{CO} + \text{OH} \rightarrow \text{CH}_3 + \text{CO} + \text{OH}$                   | $5.0(-11)$                                | c            |
| (R89)        | $\text{CH}_3\text{CO} + \text{HCO} \rightarrow \text{CH}_3\text{CHO} + \text{CO}$                    | $4.5(-11)$                                | c            |
| (R90)        | $\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$            | $6.9(-12) e^{250/T}$                      | i            |
| (R91a)       | $\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CH}_3 + \text{OH}$                                | $1.6(-10)$                                | f            |
| (R91b)       | $\text{CH}_2\text{OH} + \text{H} \rightarrow \text{H}_2\text{CO} + \text{H}_2$                       | $1.0(-11)$                                | f            |
| (R92a)       | $\text{CH}_2\text{OH} + \text{HCO} \rightarrow 2\text{H}_2\text{CO}$                                 | $3.0(-10)$                                | f            |
| (R92b)       | $\text{CH}_2\text{OH} + \text{HCO} \rightarrow \text{CH}_3\text{OH} + \text{CO}$                     | $2.0(-10)$                                | f            |
| (R93)        | $\text{CH}_2\text{OH} + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{CO}$  | $4.0(-11)$                                | f            |
| (R94)        | $\text{CH}_2\text{OH} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{H}_2\text{CO}$                   | $4.0(-12)$                                | f            |

Rate coefficients for two-body reactions are in units of  $\text{cm}^3 \text{s}^{-1}$ , those for three-body reactions are in units of  $\text{cm}^6 \text{s}^{-1}$ .

References: a, *Baulch et al.* [1976]; b, *DeMore et al.* [1987]; c, *Tsang and Hampson* [1986]; d, *Yung et al.* [1988], the listed value is for  $T = 281 \text{ K}$ ; e, *Veyret and Lescaux* [1981],  $k_{69} = 1 \times 10^{-17} \text{ cm}^3 \text{s}^{-1}$  is used in atmospheric modeling; f, *Tsang* [1987]; g, *Meier et al.* [1984]; h, *Laufer et al.* [1983] and *Patrick et al.* [1980]; i, *Atkinson and Lloyd* [1984].

Reaction (R62) is the major sink for OH radicals and also insures that the concentration of OH radicals is kept low enough so that it does not destroy the hydrocarbons which are formed later in the experiment.

In addition, there are a number of reactions leading to the formation of compounds of intermediate oxidation state. The abstraction of a hydrogen atom from a formyl radical or from formaldehyde by methoxy radical readily yields methanol,

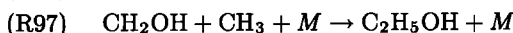
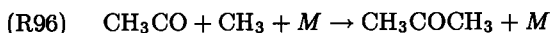
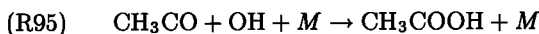


Acetaldehyde can be formed through



and a similar chain of reactions can be written for the formation of ethanol and ethane from acetaldehyde. This is a likely mechanism for their formation, since their concentrations buildup after that of acetaldehyde.

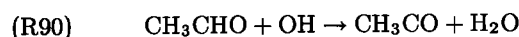
Because of the rather substantial pressure used in these experiments (about 300 torr), a large number of termolecular addition reactions involving free radicals probably occurred. Several C<sub>2</sub> hydrocarbons observed in the experiments could be formed by the following reactions,



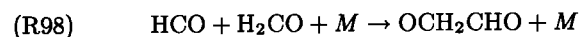
in which acetyl radicals are generated by



with a much smaller contribution from



We have also examined the formation of several higher hydrocarbon compounds not specifically identified by Bar-Nun and Chang. The addition of HCO to formaldehyde could probably produce more complex molecules via



By analogy with the reactions involving H atoms, a similar reaction chain can be written as shown in Tables 1a and 1b. These reactions could be important for producing acetaldehyde from formaldehyde. The results of the numerical simulation indicate that a complete explanation of the experimental results would have to include the chemistry of C<sub>2</sub> or even higher hydrocarbons, and this is beyond the scope of the present paper.

#### ATMOSPHERIC MODELING

Zahnle and Walker [1982] have attempted a reconstruction of the history of the solar spectrum from the Sun's T-Tauri phase onward. Their results indicate that enhancements of a few hundred, compared to modern values, in the 2000-Å region occurred during the T-Tauri phase, with much greater increases at shorter wavelengths. However, these large differences from model values lasted only about 10<sup>7</sup> years. After approximately 5 × 10<sup>8</sup> years, the solar UV output in the 2000-Å region declined to modern values, and the solar flux in the extreme UV had dropped to within a factor of 10 of the present. We have used modern values for the solar UV flux in our calculations for the sake of consistency with our choice of model atmosphere.

We have included the essential reactions in the simulations of the laboratory experiment along with other reactions in a one-dimensional model of the atmosphere. The additional reactions are listed in Table 1c. To do this, we have also tried to place some bounds on the concentrations of the major constituents of the prebiotic atmosphere. These would have been molecular nitrogen, carbon dioxide, and water vapor, with smaller quantities of reduced compounds such as H<sub>2</sub> and CO. N<sub>2</sub> would have been degassed early on, because of its low solubility in magmas. Prior to the burial of organic carbon by biological activity, the abundance of N<sub>2</sub> in the atmosphere may have been even higher than its modern value [Walker, 1976]. On the basis of the analyses of Knoll et al. [1986] for the organic carbon content of sediments and a C/N ratio of 10 [Hayes et al., 1983], we estimate that the partial pressure of N<sub>2</sub> in the atmosphere was about 1 bar throughout the Archean and much of the Proterozoic. Estimating the abundance of CO<sub>2</sub> is somewhat more difficult, although its abundance was probably higher than at present. Much higher CO<sub>2</sub> abundances could have been due to rapid degassing of meteorites (P<sub>CO<sub>2</sub></sub> = 30 bars, Holland, 1984) during accretion. The possible lack of sub-aerial weathering (P<sub>CO<sub>2</sub></sub> = 10 bars, Walker, 1986) is another possibility prior to the formation of stable continental platforms. Surface temperatures for these two cases would have been 410 and 358 K, respectively. A higher CO<sub>2</sub> abundance may have been required to keep the Earth's mean surface

temperature above freezing when the solar luminosity was lower [Owen et al., 1979; Kasting and Ackerman, 1986]. The results of Kasting and Ackerman indicate that upward of a bar of CO<sub>2</sub> may have been required to maintain the surface temperature at its present value. However, in the construction of a nominal model we have chosen to maintain the CO<sub>2</sub> partial pressure at its current value. Our reason for this choice will be discussed later. We adopt a temperature profile computed by Kasting (private communication, 1987) for an atmosphere with 1 bar CO<sub>2</sub>. The surface temperature is 295.5 K. Above the tropopause a constant temperature of 170 K is chosen. The eddy diffusivity was set equal to a constant value of 10<sup>6</sup> cm<sup>2</sup> s<sup>-1</sup> throughout the model atmosphere. The eddy diffusivity profile in the stratosphere was presumably different in the absence of an ozone layer, because the static stability of the stratosphere would have been lower, perhaps allowing more rapid exchange. A constant value was chosen in the absence of suitable analogies. The relative humidity was set equal to 50% at the surface, and this value was used to fix the water vapor abundance in the troposphere. Water vapor was calculated in the model's stratosphere and above. The rainout of soluble trace constituents was parameterized, using the treatment of Wofsy [1976]. Our use of modern values for the rainout rate of soluble gases is motivated by the results of Manabe and Bryan [1985] for increases in precipitation with increasing surface temperatures. They found changes of only about 20% in global mean rainfall rates when globally averaged surface temperatures changed by 8 K compared with current global mean surface temperature of 288 K. Because of the rather weak dependence of rainfall amount on global mean surface temperatures, along with the assumption of near-constancy of surface temperatures, we have neglected possible variations in the rainout rates.

Holland [1984] imposed limits on the rate of input of hydrogen to the early atmosphere of 1.9 × 10<sup>9</sup> to 1.9 × 10<sup>13</sup> (H atom equivalents cm<sup>-2</sup> s<sup>-1</sup>). The lower bound was set by using the mean release rate for volcanic gases over geologic time, along with the observed H<sub>2</sub> to H<sub>2</sub>O ratio in modern volcanic gases. The upper bound was set by the use of rare gas data which suggest that the maximum rate of release of volcanic gases was 100 times the mean value and by assuming a more reducing composition for the gases than at present. Actual values were probably closer to the upper limit during the first few hundred million years of Earth history. Values then declined substantially before the deposition of the earliest known sedimentary rocks about 3.8 billion years ago [Holland, 1984].

The mixing ratio of H<sub>2</sub> in the atmosphere would have been controlled by the balance between surface inputs and exospheric escape. We have assumed for the sake of simplicity that reducing power was injected into the atmosphere in the form of H<sub>2</sub>. Nearly equivalent results would have been obtained if we had used CO and H<sub>2</sub> mixtures of varying proportions (cf. equation (4)). We have used an input flux for H<sub>2</sub> of 5.0 × 10<sup>9</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>. This value was chosen because it insures that H<sub>2</sub> in the atmosphere will be in steady state with respect to exospheric loss, using modern values for the extreme ultraviolet solar flux. The corresponding mixing ratio of H<sub>2</sub> at the surface is then 1.0 × 10<sup>-3</sup>. This escape rate is governed by the rate at which H<sub>2</sub> can be converted into H atoms, by ion molecule reactions such as

TABLE 1c. Reactions Used Only for Atmospheric Modeling, With Their Preferred Rate Coefficients

| Reaction No. | Reaction                                     | Rate Constant                                       | Reference |
|--------------|----------------------------------------------|-----------------------------------------------------|-----------|
| (R1a)        | $O_2 + h\nu \rightarrow 2O$                  | 6.8(-9)                                             | a         |
| (R1b)        | $O_2 + h\nu \rightarrow O + O(^1D)$          | 1.5(-6)                                             | a         |
| (R2a)        | $O_3 + h\nu \rightarrow O_2 + O$             | 8.0(-4)                                             | b         |
| (R2b)        | $O_3 + h\nu \rightarrow O_2 + O(^1D)$        | 4.7(-3)                                             | b         |
| (R3)         | $H_2O + h\nu \rightarrow OH + H$             | 5.6(-6)                                             | c         |
| (R4)         | $H_2O_2 + h\nu \rightarrow 2OH$              | 6.7(-5)                                             | d         |
| (R5a)        | $CO_2 + h\nu \rightarrow CO + O$             | 5.6(-7)                                             | e         |
| (R5b)        | $CO_2 + h\nu \rightarrow CO + O(^1D)$        | 1.6(-7)                                             | e         |
| (R6)         | $HCO + h\nu \rightarrow CO + H$              | 6.0(-4)                                             | f         |
| (R7a)        | $H_2CO + h\nu \rightarrow HCO + H$           | 4.7(-5)                                             | g         |
| (R7b)        | $H_2CO + h\nu \rightarrow CO + H_2$          | 4.1(-5)                                             | g         |
| (R8a)        | $CH_3OH + h\nu \rightarrow CH_3 + OH$        | 3.1(-6)                                             | h         |
| (R8b)        | $CH_3OH + h\nu \rightarrow CH_2OH + H$       | 3.1(-6)                                             | h         |
| (R9a)        | $CH_3CHO + h\nu \rightarrow CH_3 + HCO$      | 4.7(-5)                                             | i         |
| (R9b)        | $CH_3CHO + h\nu \rightarrow CH_4 + CO$       | 4.1(-5)                                             | i         |
| (R11)        | $2O + M \rightarrow O_2 + M$                 | $5.2(-35) e^{900/T}$                                | j         |
| (R12)        | $O + H + M \rightarrow OH + M$               | $1.3(-29) T^{-1}$                                   | j         |
| (R13)        | $O(^1D) + O_2 \rightarrow O + O_2$           | $3.2(-11) e^{70/T}$                                 | k         |
| (R14a)       | $O(^1D) + O_3 \rightarrow 2O_2$              | 1.2(-10)                                            | k         |
| (R14b)       | $O(^1D) + O_3 \rightarrow O_2 + 2O$          | 1.2(-10)                                            | k         |
| (R15)        | $O(^1D) + H_2 \rightarrow H + OH$            | 1.0(-10)                                            | k         |
| (R16)        | $O(^1D) + CO_2 \rightarrow O + CO_2$         | $7.4(-11) e^{120/T}$                                | k         |
| (R17)        | $O(^1D) + H_2O \rightarrow 2OH$              | 2.2(-10)                                            | k         |
| (R18a)       | $O(^1D) + CH_4 \rightarrow OH + CH_3$        | 1.4(-10)                                            | k         |
| (R18b)       | $O(^1D) + CH_4 \rightarrow H_2 + H_2CO$      | 1.4(-11)                                            | k         |
| (R19)        | $O(^1D) + N_2 \rightarrow O + N_2$           | $1.8(-11) e^{110/T}$                                | k         |
| (R20)        | $O_2 + O + M \rightarrow O_3 + M$            | $2.99(-28) T^{-2.3}$                                | k         |
| (R21)        | $O_2 + H + M \rightarrow HO_2 + M$           | $k_0 = 5.24(-28) T^{-1.6}$<br>$k_\infty = 7.5(-11)$ | k         |
| (R22)        | $O_3 + O \rightarrow 2O_2$                   | $8.0(-12) e^{-2060/T}$                              | k         |
| (R23)        | $O_3 + H \rightarrow OH + O_2$               | $1.4(-10) e^{-470/T}$                               | k         |
| (R24)        | $O_3 + OH \rightarrow HO_2 + O_2$            | $1.6(-12) e^{-940/T}$                               | k         |
| (R25)        | $2H + M \rightarrow H_2 + M$                 | $1.5(-29) T^{-1.3}$                                 | j         |
| (R26)        | $H_2 + O \rightarrow OH + H$                 | $1.8(-20) T^{2.8} e^{-2980/T}$                      | j         |
| (R27)        | $OH + H + M \rightarrow H_2O + M$            | $1.38(-24) T^{-2.6}$                                | l         |
| (R28)        | $2OH \rightarrow H_2O + O$                   | $4.2(-12) e^{-240/T}$                               | k         |
| (R29)        | $2OH + M \rightarrow H_2O_2 + M$             | $6.62(-29) T^{-0.8}$                                | k         |
| (R30)        | $OH + O \rightarrow O_2 + H$                 | $2.2(-11) e^{120/T}$                                | k         |
| (R31)        | $OH + H_2 \rightarrow H_2O + H$              | $5.5(-12) e^{-2000/T}$                              | k         |
| (R32)        | $2HO_2 \rightarrow H_2O_2 + O_2$             | $2.3(-13) e^{600/T}$                                | k         |
| (R33)        | $2HO_2 + M \rightarrow H_2O_2 + O_2 + M$     | $1.7(-33) e^{1000/T}$                               | k         |
| (R34a)       | $HO_2 + H \rightarrow 2OH$                   | 7.05(-11)                                           | k         |
| (R34b)       | $HO_2 + H \rightarrow H_2 + O_2$             | 7.29(-12)                                           | k         |
| (R34c)       | $HO_2 + H \rightarrow H_2O + O$              | 3.24(-12)                                           | k         |
| (R35)        | $HO_2 + O \rightarrow OH + O_2$              | $3.0(-11) e^{200/T}$                                | k         |
| (R36)        | $HO_2 + OH \rightarrow H_2O + O_2$           | $4.6(-11) e^{230/T}$                                | k         |
| (R37)        | $HO_2 + O_3 \rightarrow OH + 2O_2$           | 1.1(-14)                                            | k         |
| (R38)        | $H_2O_2 + O \rightarrow HO_2 + OH$           | $1.4(-12) e^{-2000/T}$                              | k         |
| (R39)        | $H_2O_2 + H \rightarrow H_2O + OH$           | $4.0(-11) e^{-2000/T}$                              | j         |
| (R40)        | $H_2O_2 + OH \rightarrow HO_2 + H_2O$        | $3.3(-12) e^{-200/T}$                               | k         |
| (R41)        | $CO + O + M \rightarrow CO_2 + M$            | $6.5(-33) e^{-2184/T}$                              | p         |
| (R42a)       | $HCO + O \rightarrow CO_2 + H$               | 5.0(-11)                                            | j         |
| (R42b)       | $HCO + O \rightarrow CO + OH$                | 5.0(-11)                                            | j         |
| (R43)        | $HCO + O_2 \rightarrow HO_2 + CO$            | $3.5(-12) e^{140/T}$                                | k         |
| (R44)        | $HCO + HO_2 \rightarrow H_2O_2 + CO$         | 5.0(-11)                                            | o         |
| (R45)        | $H_2CO + O \rightarrow HCO + OH$             | $3.4(-11) e^{-1800/T}$                              | k         |
| (R46a)       | $CH_3O + O \rightarrow CH_3 + O_2$           | 2.2(-11)                                            | l         |
| (R46b)       | $CH_3O + O \rightarrow H_2CO + OH$           | 3.0(-12)                                            | l         |
| (R47)        | $CH_3O + HO_2 \rightarrow H_2CO + H_2O_2$    | 5.0(-13)                                            | j         |
| (R48)        | $CH_3O + O_2 \rightarrow H_2CO + HO_2$       | $3.9(-14) e^{-900/T}$                               | k         |
| (R49)        | $CH_3CO + O \rightarrow CH_3 + CO_2$         | 1.6(-11)                                            | j         |
| (R50)        | $CH_3CO + HO_2 \rightarrow CH_3 + CO_2 + OH$ | 5.0(-11)                                            | j         |
| (R51a)       | $CH_3OH + O \rightarrow CH_3O + OH$          | $3.22(-19) T^{2.5} e^{-1550/T}$                     | m         |
| (R51b)       | $CH_3OH + O \rightarrow CH_2OH + OH$         | $3.22(-19) T^{2.5} e^{-1550/T}$                     | m         |
| (R52)        | $CH_3 + O \rightarrow H_2CO + H$             | 1.1(-10)                                            | k         |
| (R53)        | $CH_4 + O \rightarrow CH_3 + OH$             | $1.7(-15) T^{1.5} e^{-4330/T}$                      | j         |
| (R54)        | $CH_2OH + O \rightarrow H_2CO + OH$          | 7.0(-11)                                            | m         |
| (R55)        | $CH_2OH + O_2 \rightarrow H_2CO + HO_2$      | 9.6(-12)                                            | k         |
| (R56)        | $CH_3CHO + O \rightarrow CH_3CO + OH$        | $1.8(-11) e^{-1100/T}$                              | k         |
| (R57)        | $H_2O_2 \rightarrow \text{rainout}$          | 2.3(-6)                                             | n         |
| (R58)        | $H_2CO \rightarrow \text{rainout}$           | 2.3(-6)                                             | n         |
| (R59)        | $CH_3OH \rightarrow \text{rainout}$          | 2.3(-6)                                             | n         |
| (R60)        | $CH_3CHO \rightarrow \text{rainout}$         | 2.3(-6)                                             | n         |



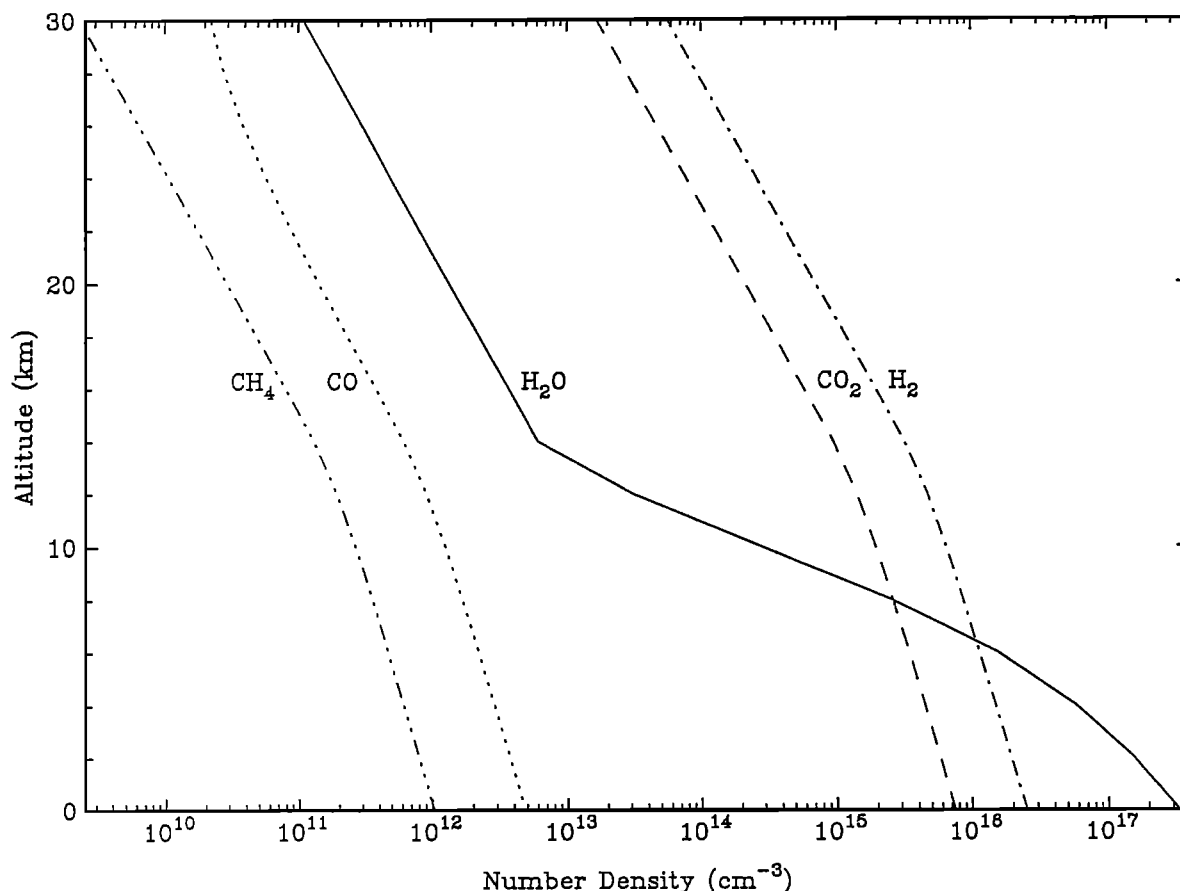
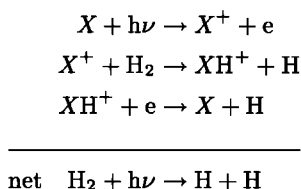


Fig. 4. Abundances of major constituents in our standard model of the prebiotic atmosphere. The bulk atmosphere consists of 1 bar N<sub>2</sub>. The mixing ratios of CO<sub>2</sub> and H<sub>2</sub> at the surface are  $3 \times 10^{-4}$  and  $1 \times 10^{-3}$ , respectively.



where  $X = \text{CO}_2$  or N<sub>2</sub> [Yung and McElroy, 1979]. If the major atmospheric constituent were CO<sub>2</sub>, exospheric temperatures would have been much lower than at the present time (about 1000 K) and may have been closer to the value observed for the Martian exosphere (about 350 K). For temperatures in the range of 300–400 K, the effusion velocity for H atoms is less than  $10^{-2} \text{ cm s}^{-1}$ , suggesting that the

thermal escape rate of hydrogen was negligible. It is unlikely that this limit was ever reached, however, because the surface flux of H<sub>2</sub> would have caused its density in the thermosphere to rise until CO<sub>2</sub> and CO were no longer the dominant constituents. We shall assume for the present that exospheric temperatures were lower than present values but higher than on Mars. We have used a range of H<sub>2</sub> surface mixing ratios varying from  $10^{-5}$  to  $10^{-3}$  in our calculations to bracket uncertainties in the extreme UV solar flux and the input rate of H<sub>2</sub> in the past.

The results of the model calculations for the major constituents in our nominal atmosphere are shown in Figure 4. The calculated mixing ratios of CO and O<sub>2</sub> at the surface are  $1.9 \times 10^{-7}$  and  $1.6 \times 10^{-19}$ , respectively. The abundance of O<sub>2</sub> in our model is consistent with those obtained in pre-

Rate coefficients for two-body reactions are in units of  $\text{cm}^3 \text{ s}^{-1}$ ; those for three-body reactions are in units of  $\text{cm}^6 \text{ s}^{-1}$ . Photodissociation coefficients (in units of  $\text{s}^{-1}$ ) refer to the optically thin region at the top of the atmosphere.

References: a, Kirby *et al.* [1979], Watanabe [1958], Ackerman [1971], Kley [1984], Hudson [1974], World Meteorological Organization (WMO) [1985], Hudson and Mahle [1972], Prather [1981], Herman and Mentall [1982], Shardanand and Rao [1977], Carver *et al.* [1977]; b, Ackerman [1971], WMO [1985], DeMore *et al.* [1985]; c, Watanabe and Zelikoff [1953], Thompson *et al.* [1963], Kley [1984], Lee and Suto [1986], Haddad and Samson [1986], Slanger and Black [1982], Stief *et al.* [1975], Wu and Judge [1981]; d, Schügers and Welge [1968], Climatic Impact Assessment Program (CIAP) [1975], DeMore *et al.* [1985]; e, Henry and McElroy [1968], Hitchcock and Brion [1980], Lewis and Carver [1983], Shemansky [1972], Nakata *et al.* [1965], Okabe [1978], Slanger and Black [1978], Lawrence [1972a,b]; f, Hochanadel *et al.* [1980]; g, DeMore *et al.* [1985]; h, Nee *et al.* [1985]; i,  $J_{9a} = J_{7a}$ ,  $J_{9b} = J_{7b}$ ; j, Tsang and Hampson [1986]; k, DeMore *et al.* [1987]; l, Ewig *et al.* [1987]; m, Tsang [1987]; n, Wofsy [1976], the listed value is its rate constant at ground; o, estimated; p, Baulch *et al.* [1976].

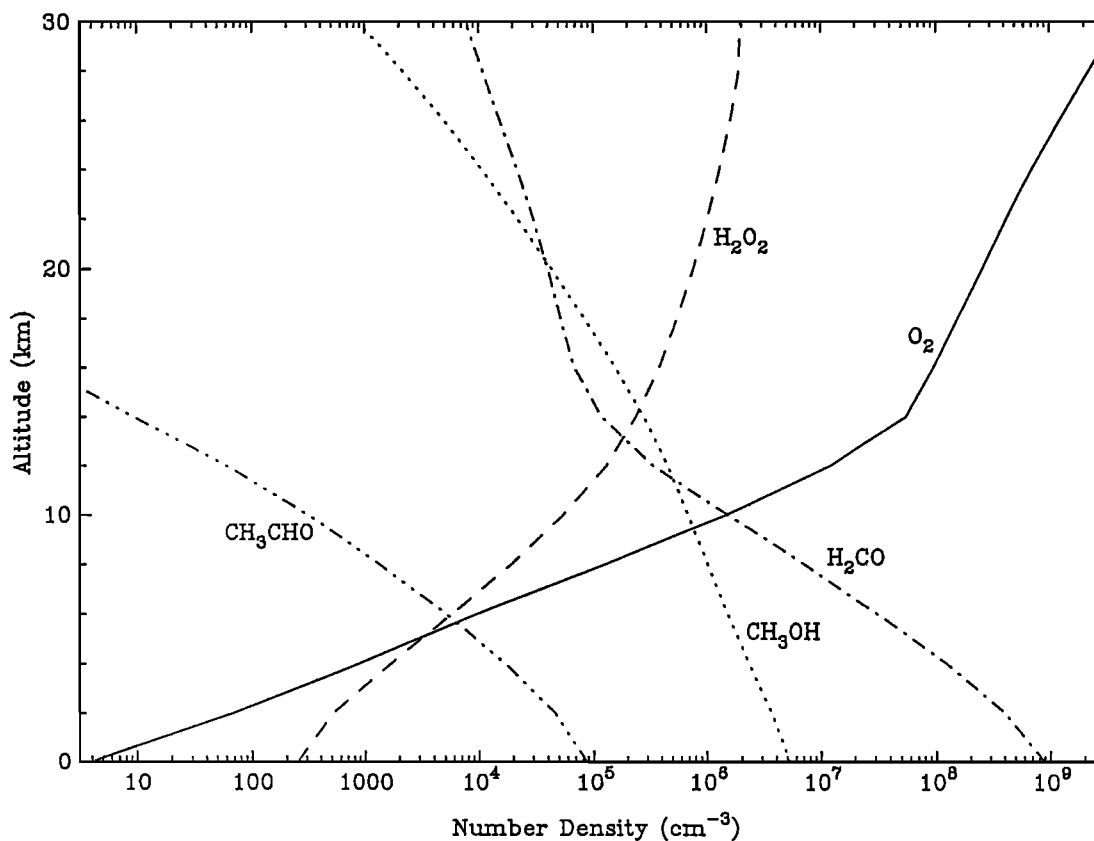


Fig. 5. Same as Figure 4, except for minor species: CH<sub>3</sub>CHO, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>CO, and CH<sub>3</sub>OH.

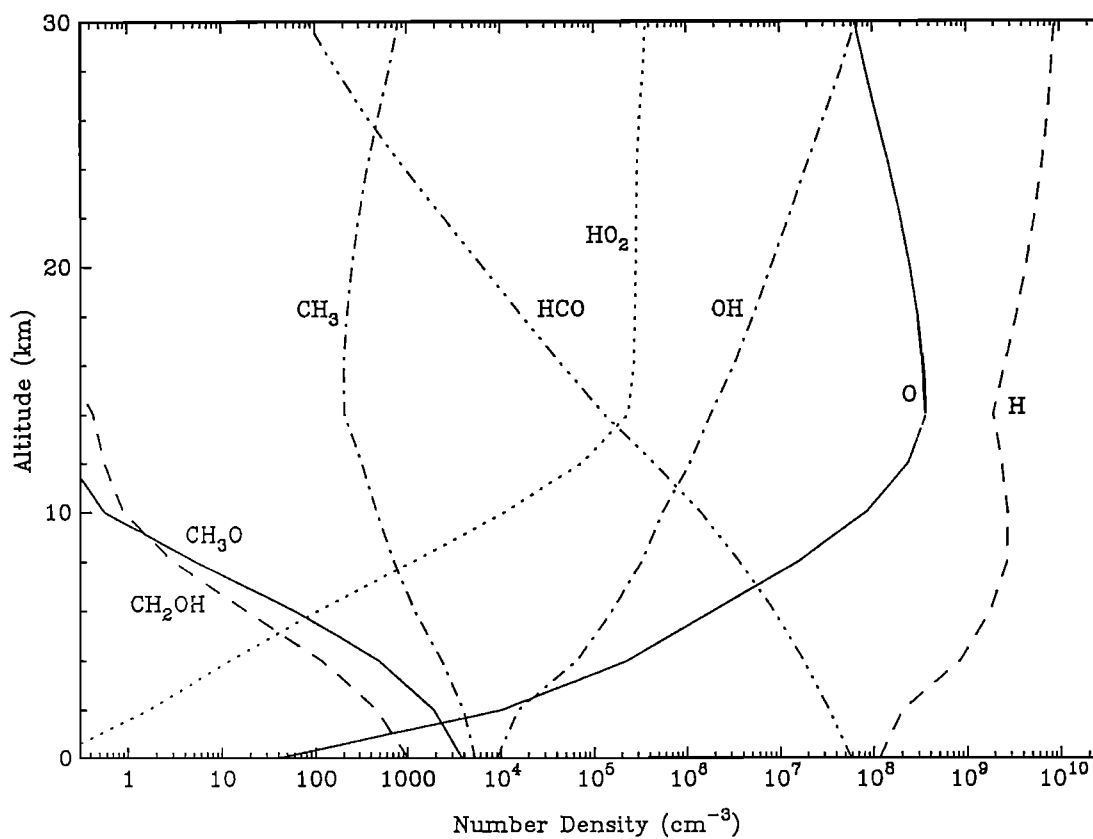


Fig. 6. Same as Figure 4, except for radical species: CH<sub>2</sub>OH, CH<sub>3</sub>O, CH<sub>3</sub>, HCO, HO<sub>2</sub>, OH, O, and H.

TABLE 2. Dependence of Surface Mixing Ratio of Major Products on the Abundance of CO<sub>2</sub> and H<sub>2</sub>

|                                      | $f_{\text{H}_2}$ |           |           |
|--------------------------------------|------------------|-----------|-----------|
|                                      | $10^{-5}$        | $10^{-4}$ | $10^{-3}$ |
| $f_{\text{CO}_2} = 3 \times 10^{-4}$ |                  |           |           |
| CO                                   | 2.3(-9)          | 2.3(-8)   | 1.9(-7)   |
| O <sub>2</sub>                       | 4.9(-18)         | 1.6(-18)  | 1.6(-19)  |
| CH <sub>4</sub>                      | 3.1(-12)         | 1.0(-9)   | 4.2(-8)   |
| $f_{\text{CO}_2} = 1 \times 10^{-3}$ |                  |           |           |
| CO                                   | 7.3(-9)          | 6.6(-8)   | 5.8(-7)   |
| O <sub>2</sub>                       | 1.8(-17)         | 1.0(-17)  | 1.6(-18)  |
| CH <sub>4</sub>                      | 1.3(-11)         | 2.0(-9)   | 3.3(-8)   |
| $f_{\text{CO}_2} = 1 \times 10^{-2}$ |                  |           |           |
| CO                                   | 8.0(-8)          | 5.7(-7)   | 4.0(-6)   |
| O <sub>2</sub>                       | 4.1(-16)         | 2.1(-15)  | 1.8(-16)  |
| CH <sub>4</sub>                      | 2.0(-10)         | 2.5(-9)   | 9.4(-9)   |

Read 2.13(-9) as  $2.13 \times 10^{-9}$ .

vious studies [e.g., *Kasting et al.*, 1979; *Levine*, 1982; and paper 1]. The calculated profiles for the less abundant molecules and the short lived radical intermediates are shown in Figures 5 and 6. The major tropospheric free radicals are H, O and HCO. The concentrations of OH radicals are kept very low because of the high concentration of CO. The basic reaction mechanism for producing formaldehyde is the same as given earlier in the discussion of the experimental results of Bar-Nun and Chang and in paper 1. The production of carbon compounds, which are more reducing than formaldehyde, is dominated by the reaction



The production of compounds such as CH<sub>4</sub>, CH<sub>3</sub>OH, and CH<sub>3</sub>CHO proceeds by the mechanisms outlined in the discussion on the experimental results. The mixing ratio of CH<sub>4</sub> at the surface in our standard model is  $4.2 \times 10^{-8}$ , or about 60 times less than the present level. Much smaller concentrations of other species, such as methanol and acetaldehyde, are also produced. A number of runs have been made to test the sensitivity of the model to the assumed abundances of CO<sub>2</sub> and H<sub>2</sub>. The results are summarized in Table 2. The rainout rates of H<sub>2</sub>CO, as summarized in Table 3, are all sizeable fractions of the estimated volcanic inputs of H<sub>2</sub> and CO<sub>2</sub> approximately 4 billion years ago, especially for the higher CO<sub>2</sub> cases. The rainout rate of H<sub>2</sub>O<sub>2</sub> is small at low levels of CO<sub>2</sub> atmospheric concentration. However, at higher CO<sub>2</sub> levels this rate is large, and in some cases it is comparable to that of H<sub>2</sub>CO, as shown in Table 3.

It is possible that CO<sub>2</sub> levels during the Archean were even higher than those shown in Tables 2 and 3. We studied a model with  $P_{\text{CO}_2} = 1$  bar and  $f_{\text{H}_2} = 1 \times 10^{-3}$  bar. The mixing ratios of CO, O<sub>2</sub>, and CH<sub>4</sub> in the model are  $6.1 \times 10^{-5}$ ,  $1.4 \times 10^{-12}$ , and  $1.2 \times 10^{-9}$ , respectively. Owing to a higher level of CO<sub>2</sub>, this model predicts more CO and O<sub>2</sub> (CO<sub>2</sub> is a source of O<sub>2</sub>) than the other models listed in Table 2. Compared with other models with the same  $f_{\text{H}_2}$

(Table 2), the abundance of CH<sub>4</sub> is lower. Again, this is due to the fact the atmosphere with higher CO<sub>2</sub> is more oxidizing and hence can destroy CH<sub>4</sub> more readily. We have found that the predictions shown in Tables 2 and 3 are highly sensitive to values chosen for the absorption cross section of H<sub>2</sub>O longward of 1960 Å and to values for the absorption cross section of CO<sub>2</sub> longward of 2040 Å for CO<sub>2</sub> levels greater than 0.01 bars. We have used the values estimated by *Kasting* [1979], which are based on a linear extrapolation from the highest wavelengths measured to optically thin values. We must emphasize that the results for the case with CO<sub>2</sub> equal to 1 bar are subject to this uncertainty. Data are needed for absorption in the long-wavelength tails of these two molecules. The difficulty with direct measurements has been that the required values are close to the Rayleigh scattering limit. Another way to assess the importance of H<sub>2</sub>O and CO<sub>2</sub> photolysis in the tails of their absorption spectra is to repeat the set of experiments performed by *Bar-Nun and Chang* [1983], using ultraviolet radiation only between 2000 and 2100 Å.

#### SUMMARY AND CONCLUSIONS

We have constructed models for the chemistry of the prebiotic Earth's atmosphere in an attempt to understand the role of the atmosphere in the production of simple organic molecules. We have used the experimental results of *Bar-Nun and Chang* [1983], both as a guide and a test of the photochemical scheme. We have been able to simulate the abundances of the major molecules observed by *Bar-Nun and Chang* [1983] in their reaction vessel to better than a factor of 2 except for formaldehyde. Our calculated yields of organic molecules more reducing than formaldehyde are systematically too low by about a factor of 2. However, it appears that their ratios to each other are correct. There are several possible explanations for this effect, including heterogeneous catalysis or an error in the values used for the rate coefficients of (R67) and (R69). However, we feel that the results are sufficiently close. In such a complex experiment agreement within a factor of 2 or 3 is hardly expected because of combined uncertainties in rate coefficient

TABLE 3. The Dependence of Rainout Rate of Formaldehyde and Hydrogen Peroxide, and the Flux of H<sub>2</sub> at the Ground on the Abundance of CO<sub>2</sub> and H<sub>2</sub>

|                                            | $f_{\text{H}_2}$ |           |           |
|--------------------------------------------|------------------|-----------|-----------|
|                                            | $10^{-5}$        | $10^{-4}$ | $10^{-3}$ |
| $f_{\text{CO}_2} = 3 \times 10^{-4}$       |                  |           |           |
| H <sub>2</sub> CO rainout rate             | 3.5(4)           | 5.3(6)    | 4.6(8)    |
| H <sub>2</sub> O <sub>2</sub> rainout rate | 8.2(6)           | 2.8(5)    | 7.8(3)    |
| H <sub>2</sub> flux                        | 5.0(9)           | 4.8(9)    | 4.1(9)    |
| $f_{\text{CO}_2} = 1 \times 10^{-3}$       |                  |           |           |
| H <sub>2</sub> CO rainout rate             | 4.0(5)           | 5.3(7)    | 2.5(9)    |
| H <sub>2</sub> O <sub>2</sub> rainout rate | 8.6(6)           | 2.5(5)    | 5.9(4)    |
| H <sub>2</sub> flux                        | 5.0(9)           | 5.3(9)    | 6.1(9)    |
| $f_{\text{CO}_2} = 1 \times 10^{-2}$       |                  |           |           |
| H <sub>2</sub> CO rainout rate             | 7.4(7)           | 2.3(9)    | 1.5(10)   |
| H <sub>2</sub> O <sub>2</sub> rainout rate | 8.4(7)           | 1.1(8)    | 1.6(8)    |
| H <sub>2</sub> flux                        | 5.1(9)           | 9.5(9)    | 2.9(10)   |

Rainout rate is in units of  $\text{cm}^{-2} \text{s}^{-1}$ ; the flux of H<sub>2</sub> is in units of  $\text{cm}^{-2} \text{s}^{-1}$ . Read 3.5(4) as  $3.5 \times 10^4$ .

data and the output of the UV lamp and possible heterogeneous effects.

Approximately 0.2% of the H<sub>2</sub>CO produced in our nominal atmospheric model is rained out and a small fraction is reduced to other organic molecules, such as CH<sub>3</sub>OH, CH<sub>4</sub>, and CH<sub>3</sub>CHO. We have neglected inputs of CO from comets and pyrolysis of carbonaceous chondrites upon impact. These processes may have temporarily increased the CO to CO<sub>2</sub> ratio and the rainout of H<sub>2</sub>CO during the tail end of accretion. CH<sub>4</sub> mixing ratios could have approached  $10^{-8}$  at the surface as the result of atmospheric photochemical reactions. Although we have focused on the role of atmospheric photochemistry for the abiotic production of simple organic molecules, this does not exclude other mechanisms, such as reactions in shock waves induced by lightning discharges and infalling meteorites, the release of hydrocarbons formed in the interstellar medium and trapped in meteorites, reactions in solution, and heterogeneous reactions. A quantitative assessment of the relative importance of these processes as well as a study of the possible coupling between all of these mechanisms is beyond the scope of the present work.

**Acknowledgments.** This work was partially supported by NASA grant NAGW-1538 to the California Institute of Technology. We thank H. D. Holland for many long and productive discussions and for exerting a benign influence on us over the years. We thank J. F. Kasting and K. J. Zahnle for many stimulating discussions. We also thank two referees for their constructive and useful comments. Contribution number 4570 from the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena.

#### REFERENCES

- Ackerman, M. Ultraviolet solar radiation related to mesospheric processes, in *Mesospheric Models and Related Experiments*, edited by G. Fiocco, pp. 149–159, Springer-Verlag, New York, 1971.
- Atkinson, R., and A. C. Lloyd, Evaluation of kinetic and mechanistic data for modeling of photochemical smog, *J. Phys. Chem. Ref. Data*, **13**, 315–444, 1984.
- Bar-Nun, A., and S. Chang, Photochemical reactions of water and carbon monoxide in Earth's primitive atmosphere, *J. Geophys. Res.*, **88**, 6662–6672, 1983.
- Bar-Nun, A., and H. Hartman, Synthesis of organic compounds from carbon monoxide and water by UV photolysis, *Origins of Life*, **9**, 93–101, 1978.
- Baulch, D. L., D. D. Drysdale, J. Duxbury, and S. J. Grant, *Evaluated Kinetic Data for High Temperature Reactions*, vol. 3: *Homogeneous Phase Reactions of the O<sub>2</sub>–O<sub>3</sub> System, the CO–O<sub>2</sub>–H<sub>2</sub> System and of Sulphur-Containing Species*, Butterworth, Stoneham, Mass., 1976.
- Carver, J. H., H. P. Gies, T. I. Hobbs, B. R. Lewis, and D. G. McCoy, Temperature dependence of the molecular oxygen photoabsorption cross section near the H Lyman  $\alpha$  line, *J. Geophys. Res.*, **82**, 1955–1960, 1977.
- Climatic Impact Assessment Program, *The natural stratosphere of 1974*, *CIAP Mono. 1*, pp. 5–184, U.S. Dep. of Transp., Washington, D.C., 1975.
- Craig, H. and J. E. Lupton, Primordial neon, helium, and hydrogen in oceanic basalts, *Earth Planet. Sci. Lett.*, **31**, 369–385, 1976.
- DeMore, W. B., J. J. Margitan, M. J. Molina, R. T. Watson, D. M. Golden, R. F. Hampson, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation 7, *JPL Publ.*, 85–87, 1985.
- DeMore, W. B., M. J. Molina, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation 8, *JPL Publ.*, 87–41, 1987.
- Ewig, F., D. Rhäsa, and R. Zellner, Kinetics, energetics and OH product yield of reaction  $\text{CH}_3\text{O} + \text{O}(^3\text{P}) \rightarrow \text{CH}_3\text{O}_2^* \rightarrow \text{Prods}$ , *Ber. Bunsenges. Phys. Chem.*, **91**, 708–717, 1987.
- Garrison, W. M., D. C. Morrison, J. G. Hamilton, A. A. Benson, and M. Calvin, Reduction of carbon dioxide in aqueous solutions by ionizing radiation, *Science*, **114**, 416–418, 1951.
- Haddad, G. N., and J. A. R. Samson, Total absorption and photoionization cross sections of water vapor between 100–1000 Å, *J. Chem. Phys.*, **84**, 6623–6626, 1986.
- Hayes, J. M., I. R. Kaplan, and K. M. Wedeking, Precambrian organic geochemistry, preservation of the record, in *The Earth's Earliest Biosphere: Its Origin and Evolution*, edited by J. W. Schopf, pp. 93–134, Princeton University Press, Princeton, New Jersey, 1983.
- Henry, R. J. W., and M. B. McElroy, Photoelectrons in planetary atmosphere, in *The Atmospheres of Venus and Mars*, edited by J. C. Brandt and M. B. McElroy, pp. 251–285, Gordon and Breach, New York, 1968.
- Herman, J. R., and J. E. Mentall, O<sub>2</sub> absorption cross section (187–225 nm) from stratospheric solar flux measurements, *J. Geophys. Res.*, **87**, 8967–8975, 1982.
- Hitchcock, A. P., and C. E. Brion, Absolute oscillator strengths for valence-shell ionic photofragmentation of N<sub>2</sub>O and CO<sub>2</sub> (8–75 eV), *Chem. Phys.*, **45**, 461–478, 1980.

- Hochanadel, C. J., T. J. Sworski, and P. J. Ogren, Ultraviolet spectrum and reaction kinetics of the formyl radical, *J. Phys. Chem.*, **84**, 231–235, 1980.
- Holland, H. D., *The Chemical Evolution of the Atmosphere and Oceans*, 582 pp., Princeton University Press, Princeton, New Jersey, 1984.
- Hubbard, J. S., J. P. Hardy, and N. H. Horowitz, Photocatalytic production of organic compounds from CO and H<sub>2</sub>O in a simulated Martian atmosphere, *Proc. Natl. Acad. Sci. USA*, **68**, 574–578, 1971.
- Hudson, R. D., Absorption cross sections of stratospheric molecules, *Can. J. Chem.*, **52**, 1465–1478, 1974.
- Hudson, R. D., and S. H. Mahle, Photodissociation rates of molecular oxygen in the mesosphere and lower thermosphere, *J. Geophys. Res.*, **77**, 2902–2914, 1972.
- Kasting, J. F., The evolution of oxygen and ozone in the Earth's atmosphere. Ph.D. thesis, Univ. of Mich., Ann Arbor, 1979.
- Kasting, J. F., and T. P. Ackerman, Climatic consequences of very high carbon dioxide levels in the Earth's early atmosphere, *Science*, **234**, 1383–1385, 1986.
- Kasting, J. F., S. C. Liu, and T. M. Donahue, Oxygen levels in the prebiological atmosphere, *J. Geophys. Res.*, **84**, 3097–3107, 1979.
- Khalil, M. A. K., and R. A. Rasmussen, Sources, sinks, and seasonal cycles of atmospheric methane, *J. Geophys. Res.*, **88**, 5131–5144, 1983.
- Kirby, K., E. R. Constantinides, S. Babeu, M. Oppenheimer, and G. A. Victor, Photoionization and photoabsorption cross sections of He, O, N<sub>2</sub>, and O<sub>2</sub> for aeronomic calculations, *At. Data Nucl. Data Tables*, **23**, 63–81, 1979.
- Kley, D., Ly( $\alpha$ ) absorption cross-section of H<sub>2</sub>O and O<sub>2</sub>, *J. Atmos. Chem.*, **2**, 203–210, 1984.
- Knoll, A. H., J. M. Hayes, A. J. Kaufman, K. Swett, and I. B. Lambert, Secular variation in carbon isotope ratios from upper protoerozoic successions of Svalbard and East Greenland, *Nature*, **321**, 832–838, 1986.
- Laufer, A. H., E. P. Gardner, T. L. Kwok, and Y. L. Yung, Computations and estimates of coefficients for hydrocarbon reactions of interest to the atmospheres of the outer solar system, *Icarus*, **56**, 560–567, 1983.
- Lawrence, G. M., Photodissociation of CO<sub>2</sub> to produce CO ( $\alpha^3\Pi$ ), *J. Chem. Phys.*, **56**, 3435–3442, 1972a.
- Lawrence, G. M., Production of O(<sup>1</sup>S) from photodissociation of CO<sub>2</sub>, *Chem. Phys.*, **57**, 5616–5617, 1972b.
- Lee, L. C., and M. Suto, Quantitative photoabsorption and fluorescence study of H<sub>2</sub>O and D<sub>2</sub>O at 50–190 nm, *Chem. Phys.*, **110**, 161–169, 1986.
- Levine, J. S., The photochemistry of the paleoatmosphere, *J. Mol. Evol.*, **18**, 161–172, 1982.
- Lewis, B. R., and J. H. Carver, Temperature dependence of the carbon dioxide photoabsorption cross section between 1200 and 1970 Å, *J. Quant. Spectrosc. Radiat. Transfer*, **30**, 297–309, 1983.
- Lowe, D. R., Stromatolites 3400–Myr old from the Archaean of western Australia, *Nature*, **284**, 441–443, 1980.
- Manabe, S., and K. Bryan, Jr., CO<sub>2</sub>-induced change in a coupled ocean-atmosphere model and its paleoclimatic implications, *J. Geophys. Res.*, **90**, 11,689–11,707, 1985.
- Meier, U., H. H. Grotheer, and T. Just, Temperature dependence and branching ratio of the CH<sub>3</sub>OH + OH reaction, *Chem. Phys. Lett.*, **106**, 97–101, 1984.
- Miller, S. L., A production of amino acids under possible primitive Earth conditions, *Science*, **117**, 528–529, 1953.
- Nakata, R. S., K. Watanabe, and F. M. Matsunaga, Absorption and photoionization coefficients of CO<sub>2</sub> in the region 580–1670 Å, *Sci. Light*, **14**, 54–71, 1965.
- Nee, J. B., M. Suto, and L. C. Lee, Photoexcitation processes of CH<sub>3</sub>OH: Rydberg states and photofragment fluorescence, *Chem. Phys.*, **98**, 147–155, 1985.
- Okabe, H., *Photochemistry of Small Molecules*, Wiley-Interscience, New York, 1978.
- Owen, T., R. D. Cess, and V. Ramanathan, Early Earth: An enhanced carbon dioxide greenhouse to compensate for reduced solar luminosity, *Nature*, **277**, 640–642, 1979.
- Patrick, R., M. J. Pilling, and G. J. Rogers, A high pressure rate constant for CH<sub>3</sub> + H and an analysis of the kinetics of the CH<sub>3</sub> + H → CH<sub>4</sub> reaction, *Chem. Phys.*, **59**, 279–291, 1980.
- Pinto, J. P., G. R. Gladstone, and Y. L. Yung, Photochemical production of formaldehyde in Earth's primitive atmosphere, *Science*, **210**, 183–185, 1980.
- Prather, M. J., Ozone in the upper stratosphere and mesosphere, *J. Geophys. Res.*, **86**, 5325–5338, 1981.
- Ringwood, A. E., *Origin of the Earth and Moon*, 295 pp., Springer, New York, 1979.
- Schopf, J. W., J. M. Hayes, and M. R. Walter, Evolution of Earth's earliest ecosystems: Recent progress and unsolved problems, in *The Earth's Earliest Biosphere: Its Origin and Evolution*, edited by J. W. Schopf, pp. 361–384, Princeton University Press, Princeton, New Jersey, 1983.
- Schügers, M., and K. H. Welge, Absorptionskoeffizient von H<sub>2</sub>O<sub>2</sub> und N<sub>2</sub>H<sub>4</sub> zwischen 1200–2000 Å, *Z. Naturforsch.*, **23a**, 1508–1510, 1968.
- Shardanad and A. D. P. Rao, Collision-induced absorption of O<sub>2</sub> in the Herzberg continuum, *J. Quant. Spectrosc. Radiat. Transfer*, **17**, 433–439, 1977.
- Shemansky, D. E., CO<sub>2</sub> extinction coefficient 1700–3000 Å, *J. Chem. Phys.*, **56**, 1582–1587, 1972.
- Slinger, T. G., and G. Black, CO<sub>2</sub> photolysis revised, *J. Chem. Phys.*, **68**, 1844–1849, 1978.
- Slinger, T. G., and G. Black, Photodissociative channels at 1216 Å for H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub>, *J. Chem. Phys.*, **77**, 2432–2437, 1982.
- Sodeau, J. R., and E. C. K. Lee, Intermediacy of hydroxymethylene (HCOH) in the low temperature matrix photochemistry of formaldehyde, *Chem. Phys. Lett.*, **57**, 71–74, 1978.
- Stevenson, D. J., The nature of the Earth prior to the rock record: The Hadean Earth, in *The Earth's Earliest Biosphere: Its Origin and Evolution*, edited by J. W. Schopf, pp. 32–40, Princeton University Press, Princeton, New Jersey, 1983.
- Stief, L. J., W. A. Payne, and R. B. Klemm, A flash photolysis-resonance fluorescence study of the formation of O(<sup>1</sup>D) in the photolysis of water and the reaction of O(<sup>1</sup>D) with H<sub>2</sub>, Ar, and He, *J. Chem. Phys.*, **62**, 4000–4008, 1975.
- Thompson, B. A., P. Hartek, and R. R. Reeves, Jr., Ultraviolet absorption coefficients of CO<sub>2</sub>, CO, O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>O, NH<sub>3</sub>, NO, SO<sub>2</sub>, and CH<sub>4</sub> between 1850 and 4000 Å, *J. Chem. Phys.*, **68**, 6431–6436, 1963.
- Tsang, W., Chemical kinetics data base for combustion chemistry, 2, Methanol, *J. Phys. Chem. Ref. Data*, **16**, 471–508, 1987.
- Tsang, W., and R. F. Hampson, Chemical kinetic data base for combustion chemistry, 1, Methane and related compounds, *J. Phys. Chem. Ref. Data*, **15**, 1087–1279, 1986.
- Veyret, B., and R. Lescaux, Absolute rate constants for the reactions of HCO with O<sub>2</sub> and NO from 298 to 503 K, *J. Phys. Chem.*, **85**, 1918–1922, 1981.
- Walker, J. C. G., Implications for atmospheric evolution of the inhomogeneous accretion model of the origin of the Earth, in *The Early History of the Earth*, edited by B. F. Windley, pp. 535–546, John Wiley, New York, 1976.
- Walker, J. C. G., Carbon dioxide on the early Earth, *Origins Life*, **16**, 117–127, 1986.
- Walter, M. R., Palaeobiology of Archaean stromatolites (abstract), in *Second International Archaean Symposium (Perth)*, Canberra, edited by J. E. Glover and D. I. Groves, pp. 22–23, Australian Academy of Science, Canberra, 1980.
- Watanabe, K., Ultraviolet absorption processes in the upper atmosphere, *Adv. Geophys.*, **5**, 153–221, 1958.
- Watanabe, K., and M. Zelickoff, Absorption coefficients of water vapor in the vacuum ultraviolet, *J. Opt. Soc. Am.*, **43**, 753–755, 1953.
- Wofsy, S. C., Interactions of CH<sub>4</sub> and CO in the Earth's atmosphere, *Annu. Rev. Earth Planet. Sci.*, **4**, 441–469, 1976.
- World Meteorological Organization, Atmospheric Ozone, *WMO Rep. 16*, Geneva, Switzerland, 1985.
- Wu, C. Y. R., and D. L. Judge, Lyman- $\alpha$  fluorescence from hydrogen photofragments of CH<sub>4</sub> and H<sub>2</sub>O, *Chem. Phys.*, **75**, 172–178, 1981.
- Yung, Y. L., and M. B. McElroy, Fixation of nitrogen in the prebiotic atmosphere, *Science*, **203**, 1002–1004, 1979.
- Yung, Y. L., W. A. Drew, J. P. Pinto, and R. R. Friedl, Estimation of the reaction rate for the formation of CH<sub>3</sub>O from H + H<sub>2</sub>CO: Implication for chemistry in the solar system, *Icarus*, **79**, 516–526, 1988.

Zahnle, K. J., and J. C. G. Walker, The evolution of solar ultraviolet luminosity, *Rev. Geophys.*, **20**, 280–292, 1982.

Y. L. Yung, Division of Geological and Planetary Sciences, 170-25, California Institute of Technology, Pasadena, CA 91125.

---

J. P. Pinto, Geophysical Fluid Dynamics Laboratory, Princeton University, Princeton, NJ 08542.

J. -S. Wen, Department of Chemistry, B-017, University of California, San Diego, La Jolla, CA 92093.

(Received June 6, 1988;  
(revised February 14, 1989;  
accepted February 14, 1989.)